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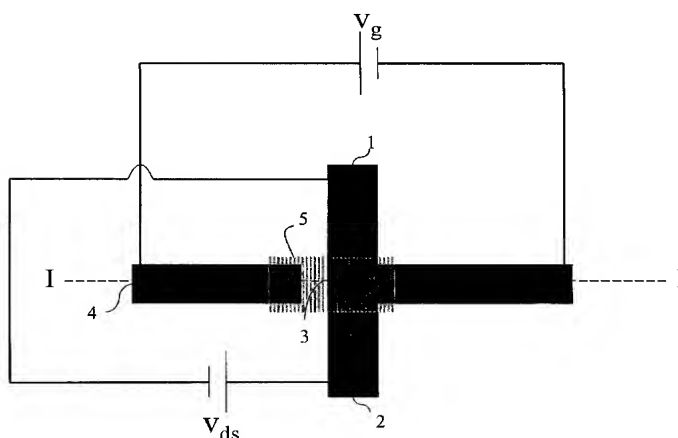
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(54) Title: ELECTROCHEMICAL SENSOR



(57) Abstract: An electrochemical sensor device is provided, comprising a source contact, a drain contact, at least one gate electrode, an electrochemically active element arranged between, and in direct electrical contact with, the source and drain contacts, which electrochemically active element comprises a transistor channel and is of a material comprising an organic material having the ability of electrochemically altering its conductivity through change of redox state thereof, optionally comprising an ion-selective layer comprising a material which is selective for at least one ionic species, which layer is in direct electrical contact with the electrochemically active element, and comprising a solidified electrolyte in direct electrical contact with the electrochemically active element or ion-selective layer and said at least one gate electrode and interposed between them in such a way that electron flow between the electrochemically active element and said gate electrode(s) is prevented. In the device, flow of electrons between source contact and drain contact is controllable by means of a voltage applied to said gate electrode(s), and controllable by means of a change in concentration of said ionic species in the solidified electrolyte. Also provided are processes for the production of such devices.



WO 03/046540 A1



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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

ELECTROCHEMICAL SENSORField of the invention

The present invention relates to electrochemical devices, in particular to printable sensors based on electrochemical transistor or diode devices which utilise  
5 conducting organic materials.

Background of the invention

Semiconducting and conducting organic materials, both polymers and molecules, have successfully been  
10 included in a large range of electronic devices, e g electrochemical devices, for instance as dynamic colorants in smart windows and in polymer batteries. Reversible doping and de-doping involving mobile ions switches the material between different redox states.

15 Use has been made of semiconducting polymers for the realisation of field effect transistor (FET) devices. The transistor channel of these devices comprises the semiconducting polymer in question, and their function is based on changes in charge carrier characteristics in the  
20 semiconducting polymer, caused by an externally applied electric field. In such transistors, the polymer is used as a traditional semiconductor, in that the electric field merely redistributes charges within the polymer material. One such transistor has been realised, which is  
25 adapted for miniaturisation and can be used for the production of integrated circuits consisting entirely of polymer material (PCT publication WO99/10939). A stack of sandwiched layers is described, with either a top-gate or a bottom-gate structure. A transistor device with a  
30 similar architecture, also using a polymer as semiconducting material in the channel of the transistor, is described in the European patent application EP1041653.

Another type of transistor device based on organic materials utilises electrochemical redox reactions in the organic material. These devices comprise an electrolyte and a conducting polymer that can be switched between an oxidised and a reduced state. One of these oxidation states then corresponds to low, preferably zero, conductivity in the material, whereas the other oxidation state corresponds to a high conductivity relative to the first state. Electrochemical transistor devices have been used as sensors, e g for detection of oxidant in a solution (see, for review, Baughman and Shacklette, Proceedings of the Sixth Europhysics Industrial Workshop (1990), p 47-61). Furthermore, a transistor of the electrochemical type is reported in Rani et al, J Solid State Electrochem (1998), vol 2, p 99-101. The gate electrode architecture in this prior art transistor is shown in Figure 1 of this reference.

Problems with sensors based on electrochemical transistor devices of the prior art include the fact that they are difficult and expensive to manufacture. In particular, no sensor based on an electrochemical transistor or diode device has been disclosed which is capable of being mass produced. Furthermore, the practical use of e g prior art electrochemical transistor devices has been hampered by their comparatively high power consumption. Furthermore, materials used in prior art devices suffer from a lack of environmental friendliness, processability and economic production possibilities. There is therefore a need for new and improved sensors based on electrochemical transistor and diode devices.

#### Summary of the invention

One of the objects of the present invention is then to meet this demand, by developing the art of electrochemical sensor devices, and by providing a device

with handling, production, disposal and other characteristics superior to those of the prior art.

Another object of the present invention is to provide an electrochemical sensor device which can be deposited on a large range of different rigid or flexible substrates by conventional printing methods.

Yet another object of the present invention is to provide an environmentally safe electrochemical sensor device, so that the disposal of the device, along with any support onto which it has been deposited, doesn't give rise to handling problems, and so that no safety restrictions have to be imposed on the use of the device.

Still another object of the present invention is to make possible new applications of conducting organic materials, using several different properties of such materials in combination.

A further object of the invention is to provide processes for the production of such devices, which processes utilise conventional printing methods or other deposition techniques that are well known, relatively unexpensive and easily scaled up.

The aforementioned objects are met by an electrochemical sensor device as defined in the independent claims. Specific embodiments of the invention are defined in the dependent claims. In addition, the present invention has other advantages and features apparent from the detailed description below.

The basic insight underlying the present invention is that the above objects may be met by the provision of a particular form of transistor device, which has been provided with sensing means. The transistor device operates through electrochemical reactions, which alter the conductivity of a transistor channel within an electrochemically active element. These electrochemical reactions are controlled by the application or removal of gate voltage to the transistor. In forming a sensor device based on such a transistor, the electrochemical

reactions governing the conductivity are made to respond not only to the gate voltage, but also to environmental parameters in the electrolyte surrounding the transistor channel, or to environmental parameters outside of the device taken as a whole. Particularly, changes in such environmental parameters may be measured. Examples of such environmental parameters will be given in the following description, which description will start with a description of the essential features comprised in aspects of the electrochemical sensor device according to the invention.

Thus, in one of its aspects, the invention provides a supported or self-supporting electrochemical sensor device, which comprises:

- a source contact,
- a drain contact,
- at least one gate electrode,
- an electrochemically active element arranged between, and in direct electrical contact with, the source and drain contacts, which electrochemically active element comprises a transistor channel and is of a material comprising an organic material having the ability of electrochemically altering its conductivity through change of redox state thereof,
- an ion-selective layer comprising a material which is selective for at least one ionic species, which layer is in direct electrical contact with the electrochemically active element, and
- a solidified electrolyte in direct electrical contact with the ion-selective layer and said at least one gate electrode and interposed between them in such a way that electron flow between the electrochemically active element and said gate electrode(s) is prevented,

whereby flow of electrons between source contact and drain contact is controllable by means of a voltage

applied to said gate electrode(s), and controllable by means of a change in concentration of said ionic species in the solidified electrolyte.

The architecture of the electrochemical sensor device according to the invention is advantageous in that it makes possible the realisation of a layered sensor device with only a few layers, having for example one patterned layer of material comprising a conducting organic material, which layer comprises source and drain contacts and gate electrode(s), as well as the electrochemically active element. The source and drain contacts and the electrochemically active element are then preferably formed by one continuous piece of said material. The source and drain contacts could alternatively be formed from another electrically conducting material in direct electrical contact with the electrochemically active element. The gate electrode(s) may also be of another electrically conducting material. To provide for the necessary electrochemical reactions, whereby the conductivity in the active element is changed, a solidified electrolyte is arranged so that it is in direct electrical contact with the gate electrode(s), as well as with the active element via the ion-selective layer. It is also possible for the direct electrical contact of the electrolyte with the gate electrode(s) to be provided via an ion-selective layer.

It is to be understood, that the ion-selective layer need not cover the entire electrochemically active element. According to some embodiments, the ion-selective layer only covers a transistor channel or a redox sink, or selected parts of these. It is furthermore possible for the ion-selective layer to be made up by different materials at different regions. For example, the transistor channel might be covered by a first ion-selective layer material, having some particular properties, while the redox sink is covered by a second

ion-selective layer material, having properties differing from the properties of the first layer.

In a preferred embodiment, the source and drain contacts and gate electrode(s), as well as the active  
5 element, are all arranged to lie in a common plane, further simplifying production of the device by ordinary printing methods. Thus, the electrochemical device according to this embodiment of the invention uses a lateral device architecture. Layers of solidified  
10 electrolyte and ion-selective material can advantageously be deposited so that they cover, at least partly, the gate electrode(s) as well as covering the electrochemically active element.

The layer of solidified electrolyte may be  
15 continuous or interrupted, depending partly on which of two main types of sensor architectures is to be realised (see below).

The electrochemical sensor device according to the invention allows for control of electron flow between  
20 source and drain contacts. The conductivity of the transistor channel of the electrochemically active element can be modified, through altering of the redox state of the organic material therein. This is achieved by application of a voltage to the gate electrode(s),  
25 which generates an electric field in the electrolyte. In the contact area between electrolyte and electrochemically active element, electrochemical redox reactions take place, which change the conductivity of the organic material. Either the organic material in the  
30 transistor channel is modified from a conducting state to a non-conducting state as a result of said redox reactions, or it is modified from a non-conducting to a conducting state.

Such a change in transistor characteristics, e g  
35 conductivity, of the organic material may also be brought about by changes in concentration in the electrolyte of the ion species for which the ion-selective layer is



selective. Obviously, the concentration in the electrolyte of the ion species for which the ion-selective layer is selective refers to the concentration of effective or active ion species, i.e. ion species which could participate in the intended electrochemical reaction(s) and/or in the current transport. Thus, in addition to the actual concentration of the active ion species, the concentration also depends on for example their mobility.

10       The function of the ion-selective layer is to separate the active element on which it is deposited, e.g. a transistor channel or a redox sink from the electrolyte, and to only allow specific ionic species to migrate between electrolyte and active element. Ions that are allowed to migrate through the ion-selective layer modulate the transistor characteristics, such as the conductivity, of the organic material of the transistor channel. Based on this modulation, the concentration of the specific ionic species in the electrolyte may be measured.

In another aspect, the invention provides a supported or self-supporting electrochemical sensor device comprising:

- a source contact,
- 25       - a drain contact,
- at least one gate electrode,
- an electrochemically active element arranged between, and in direct electrical contact with, the source and drain contacts, which electrochemically active element comprises a transistor channel and is of a material comprising an organic material having the ability of electrochemically altering its conductivity through change of redox state thereof,
- 30       - a solidified electrolyte in direct electrical contact with the electrochemically active element and said at least one gate electrode and
- 35

interposed between them in such a way that electron flow between the electrochemically active element and said gate electrode(s) is prevented, which solidified electrolyte comprises a material  
5 whose ion transport behaviour is responsive to a change in an environmental parameter,

whereby flow of electrons between source contact and drain contact is controllable by means of a voltage applied to said gate electrode(s), and controllable by  
10 means of a change in said environmental parameter.

Thus, in this aspect as in the previously described aspect, the conductivity in the organic material of the electrochemically active element is modulated through application of a gate voltage. Whereas the previously  
15 described aspect comprises an ion-selective layer for the determination of ion species concentration in the electrolyte, this aspect of the invention, however, utilises as sensing means an electrolyte which itself is responsive to changes in environmental parameters. Among  
20 such parameters are humidity, temperature, light, pressure, the concentration in the surrounding air of gaseous contaminant and ion concentration. The ion conductivity in the electrolyte is altered in response to changes in the environmental parameter, which alteration  
25 in turn gives rise to a change in the transistor characteristics, e g the conductivity of the transistor. This change in ion conductivity thus provides a measure of the environmental parameter in question. The environmental parameter might in fact be the ion  
30 concentration in a medium surrounding the device, for example the ion concentration in a liquid in which the sensor device is submerged, or in a drop of liquid placed in contact with the electrolyte. In such case, the surrounding medium might donate ions to the electrolyte,  
35 resulting in an increased ion concentration in the electrolyte which in turn accelerates electrochemical reactions. It is thus possible to monitor the

concentration of ions in the surrounding medium. In case a specific type of ions are to be monitored, the device can be provided with an ion-selective layer or ion filter covering the solidified electrolyte and prohibiting  
5 unintended donation of ions from being donated to the electrolyte while permitting donation of the specific type of ions.

It will be apparent to the skilled man that the electrochemical sensor device of the present invention  
10 may be based on a transistor device, which has been provided with means for detecting an ion concentration change in the electrolyte (the first aspect of the invention) or a change in an environmental parameter affecting the conductivity of the electrolyte (the second  
15 aspect of the invention). Alternatively, the sensor may be a diode device. Different embodiments of the electrochemical transistor device upon which the sensor of the invention may be based will now be explained. The description of changes in conductivity in response to a  
20 gate voltage is also applicable to the cases where changes in ion concentration or an environmental parameter occur. For the purposes of accurate measurements using the sensor device of the invention, it is preferable that the gate voltage is kept constant when  
25 such measurements are performed.

The sensor might be operated as follows. First, it is exposed to the environment it is supposed to sense upon. Thereafter, a voltage is applied across two gate electrodes, and the electrical resistance between the  
30 drain and source contacts is measured. The applied gate voltage can be either a static voltage or a pulsed voltage. A static voltage is a constant voltage applied for a certain amount of time, for example 1 V applied for 2 seconds or to the instant the sensor has reached an  
35 equilibrium state. During these two seconds, the electric characteristics between the source and drain contacts are determined. A pulsed voltage is an alternating voltage

applied for a certain amount of time. The alternating voltage might for example alternate at 1 Hz between -1 V and 1 V. To make a sensor measurement using pulsed voltage, the pulsed voltage is applied for a certain number of cycles, for example 2 or 3, and the electric characteristics between the source and drain contacts are determined. In some circumstances, the pulsed measurement can be expected to be faster and render more information than would a static measurement. Depending on the precise patterning of the conducting organic material and the electrolyte, the electrochemical transistor device of the invention can either be of a bi-stable or a dynamic type. In the bi-stable transistor embodiment, a voltage applied to the gate electrode(s) leads to a change in conductivity in the transistor channel that is maintained when the external circuit is broken, i.e. when the applied voltage is removed. The electrochemical reactions induced by the applied voltage can not be reversed, since the electrochemically active element and the gate electrode(s) are not in direct electrical contact with each other, but separated by electrolyte and optionally an ion-selective layer. In this embodiment, the transistor channel can be switched between non-conducting and conducting states using only small, transient gate voltages. The bi-stable transistor can be kept in an induced redox state for days, and, in the most preferred, ideal case, indefinitely.

Thus, the bi-stable transistor embodiment of the present invention offers a memory function, in that it is possible to switch it on or off using only a short voltage pulse applied to the gate electrode. The transistor stays in the conducting or non-conducting redox state even after the applied voltage has been removed. A further advantage with such bi-stable transistors is that close to zero-power operation is made possible, since the short voltage pulses applied to the gate need not be larger than a fraction of the gate

voltages needed for operation of a corresponding dynamic device.

In the dynamic transistor embodiment, the change in the redox state of the material is reversed spontaneously upon withdrawal of the gate voltage. This reversal is obtained through the provision of a redox sink volume adjacent to the transistor channel in the electrochemically active element. Also, a second gate electrode is provided, and arranged so that the two gate electrodes are positioned on either side of the electrochemically active element, one closer to the transistor channel, and the other closer to the redox sink volume. Both gate electrodes are separated from the electrochemically active element by electrolyte and optionally an ion-selective layer. Application of a voltage between the two gate electrodes results in the electrochemically active element being polarised, whereby redox reactions take place in which the organic material in the transistor channel is reduced while the organic material in the redox sink volume is oxidised, or vice versa. Since the transistor channel and the redox sink volume are in direct electrical contact with each other, withdrawal of gate voltage leads to a spontaneous reversal of the redox reactions, so that the initial conductivity of the transistor channel is re-established. It is to be stressed that in contrast to electrochemical transistors of the prior art, dynamic transistors according to this embodiment of the present invention revert spontaneously to the initial conductivity state without the need for a reversing bias.

The electrochemical sensor device according to the invention is also particularly advantageous in that it can be easily realised on a support, such as polymer film or paper. Thus, the different components can be deposited on the support by means of conventional printing techniques such as screen printing, offset printing, ink-jet printing and flexographic printing, or coating

techniques such as knife coating, doctor blade coating, extrusion coating and curtain coating, such as described in "Modern Coating and Drying Technology" (1992), eds E D Cohen and E B Guttoff, VCH Publishers Inc, New York, NY, USA. In those embodiments of the invention that utilise a conducting polymer as the organic material (see below for materials specifications), this material can also be deposited through *in situ* polymerisation by methods such as electropolymerisation, UV-polymerisation, thermal polymerisation and chemical polymerisation. As an alternative to these additive techniques for patterning of the components, it is also possible to use subtractive techniques, such as local destruction of material through chemical or gas etching, by mechanical means such as scratching, scoring, scraping or milling, or by any other subtractive methods known in the art. An aspect of the invention provides such processes for the manufacture of an electrochemical sensor device from the materials specified herein.

However, the invention is not limited to supported devices, as the contacts and electrode(s), electrochemically active element, ion-selective layer and electrolyte can be arranged in such a way that they support each other. An embodiment of the invention thus provides for a self-supporting device. According to some embodiments of the invention, the electrochemical sensor device is encapsulated, in part or entirely, for protection of the device. The encapsulation retains any solvent needed for e g the solidified electrolyte to function, and also keeps oxygen from disturbing the electrochemical reactions in the device. Encapsulation can be achieved through liquid phase processes. Thus, a liquid phase polymer or organic monomer can be deposited on the device using methods such as spray-coating, dip-coating or any of the conventional printing techniques listed above. After deposition, the encapsulant can be hardened for example by ultraviolet or infrared

irradiation, by solvent evaporation, by cooling or through the use of a two-component system, such as an epoxy glue, where the components are mixed together directly prior to deposition. Alternatively, the  
5 encapsulation is achieved through lamination of a solid film onto the electrochemical transistor device. In preferred embodiments of the invention, in which the components of the electrochemical transistor device are arranged on a support, this support can function as the  
10 bottom encapsulant. In this case encapsulation is made more convenient in that only the top of the sheet needs to be covered with liquid phase encapsulant or laminated with solid film.

It is furthermore possible for the encapsulating  
15 layer to have ion-selective properties. Thus, the encapsulating layer can also serve as an ion-selective layer or ion filter in order to selectively permit donation of specific ions from a surrounding medium to the solidified electrolyte, as described earlier.

20 It is furthermore possible for the substrate layer to have ion-selective properties. Thus, according to some embodiments of the invention, the substrate layer also serves as an ion-selective layer.

As is readily appreciated by the skilled person, and  
25 in analogy to conventional field effect transistors, the electrochemical sensor transistor device of the invention may readily be made to function as a sensor diode device through short-circuiting of the gate electrode and source contact, or of the gate electrode and drain contact.

30 The invention will now be further described with reference to specific embodiments thereof and to specific materials, as well as to experiments conducted. This detailed description is intended for purposes of exemplification, not for limitation in any way of the  
35 scope of the invention as claimed.

Brief description of the drawings

Figure 1. Schematic structure of one embodiment of a bi-stable transistor, showing (A) a top view and (B) a cross-section along I-I in A.

5        Figure 2. Schematic structure of a dynamic transistor, showing (A) a top view and (B) a cross-section along I-I in A.

10        Figure 3. Schematic structure of another embodiment of a bi-stable transistor, showing (A) a top view and (B) a cross-section along I-I in A.

Figure 4.  $I_{ds}$  vs  $V_{ds}$  characteristics at various gate voltages for experiments carried out on a bi-stable transistor as shown in Figure 1. The inset shows  $I_d$  vs  $V_g$  at constant  $V_{ds}$  ( $V_{ds}=2.0$  V).

15        Figure 5.  $I_{ds}$  vs  $V_{ds}$  characteristics at various gate voltages for experiments carried out on a dynamic transistor. The inset shows  $I_d$  vs  $V_g$  at constant  $V_{ds}$  ( $V_{ds}=2.0$  V).

20        Figure 6. Schematic structure of one embodiment of a sensor device according to the invention, showing (A) a top view and (B) a cross-section along I-I in A.

Figure 7. **a.** Schematic view of a humidity sensor according to the invention, based on a transistor device. S: source; D: drain; G1: gate 1; G2: gate 2; All area, except the layer of proton conductor and the S, D, G1 and G2 contacts, is covered with SU-8. **b.** Cross section through the channel of the transistor. **c.** Schematic view of a humidity sensor according to the invention, based on a diode device. A: anode; C: cathode. All of the area, except the layer of proton conductor and the A and C contacts, is covered with plastic foil. **d.** Cross section through the active area of the diode.

25  
30

Figure 8. A) Measurements upon the diode structure. B) Measurements upon the transistor structure. The variation in the real humidity in the chamber is clearly seen as variations in the current through the diode and the transistor. T: temperature; RH: relative humidity;

35



real: the real value measured in the climate chamber;  $I_f$ : current through the diode;  $I_{DS}$ : current between source and drain;  $I_g$ : current through the gate contact.

5 Detailed description of preferred embodiments

**Definitions**

Bi-stable electrochemical transistor: an electrochemical transistor device in which the transistor  
10 channel retains its redox state (and hence its conductivity characteristics) when the gate voltage is removed.

Dynamic electrochemical transistor: an electrochemical transistor device in which the transistor  
15 channel spontaneously returns to its initial redox state (and hence to its initial conductivity characteristics) when the gate voltage is removed.

Source contact: an electrical contact which provides charge carriers to a transistor channel.

20 Drain contact: an electrical contact which accepts charge carriers from a transistor channel.

Gate electrode: an electrical contact of which any fraction of the surface area is in direct electrical contact with solidified electrolyte, and therefore in  
25 ionic contact with the electrochemically active element.

Electrochemically active element: an "electro-chemically active element" according to the present invention, is a piece of a material comprising an organic material having a conductivity that can be  
30 electrochemically altered through changing of the redox state of said organic material. The electrochemically active element is in ionic contact with at least one gate electrode via a solidified electrolyte and optionally an ion-selective layer. The electrochemically active element  
35 may furthermore be integrated with each of the source and drain contacts individually or with both of them, being composed of the same or different materials. The

electrochemically active element in the electrochemical sensor devices of the invention comprises a transistor channel, and may furthermore comprise a redox sink volume.

5 Transistor channel: the "transistor channel" of the electrochemically active element establishes electrical contact between source and drain contacts.

Redox sink volume: in certain embodiments of the invention, the electrochemically active element further  
10 comprises a "redox sink volume". This is a part of the electrochemically active element adjacent to and in direct electrical contact with the transistor channel, which can provide or accept electrons to or from the transistor channel. Thus, any redox reactions within the  
15 transistor channel are complemented by opposing reactions within the redox sink volume.

Redox state: when reference is made to changes in the "redox state" of the electrochemically active element, this is intended to include cases where the  
20 organic material in the electrochemically active element is either oxidised or reduced, as well as cases where there is a redistribution of charges within the electrochemically active element, so that one end (e g the transistor channel) is reduced and the other end (e g  
25 the redox sink volume) is oxidised. In the latter case, the electrochemically active element as a whole retains its overall redox state, but its redox state has nevertheless been changed according to the definition used herein, due to the internal redistribution of charge  
30 carriers.

Direct electrical contact: Direct physical contact (common interface) between two phases (for example electrode and electrolyte) that allows for the exchange of charges through the interface. Charge exchange through  
35 the interface can comprise transfer of electrons between electrically conducting phases, transfer of ions between ionically conducting phases, or conversion between

electronic current and ionic current by means of electrochemistry at an interface between for example electrode and electrolyte or electrolyte and electrochemically active element, or by occurrence of  
5 capacitive currents due to the charging of the Helmholtz layer at such an interface.

Solidified electrolyte: for the purposes of the invention, "solidified electrolyte" means an electrolyte, which at the temperatures at which it is used is  
10 sufficiently rigid that particles/flakes in the bulk therein are substantially immobilised by the high viscosity/rigidity of the electrolyte and that it doesn't flow or leak. In the preferred case, such an electrolyte has the proper rheological properties to allow for the  
15 ready application of this material on a support in an integral sheet or in a pattern, for example by conventional printing methods. After deposition, the electrolyte formulation should solidify upon evaporation of solvent or because of a chemical cross-linking  
20 reaction, brought about by additional chemical reagents or by physical effect, such as irradiation by ultraviolet, infrared or microwave radiation, cooling or any other such method. The solidified electrolyte preferably comprises an aqueous or organic solvent-  
25 containing gel, such as gelatine or a polymeric gel. However, solid polymeric electrolytes are also contemplated and fall within the scope of the present invention. Furthermore, the definition also encompasses liquid electrolyte solutions soaked into, or in any other  
30 way hosted by, an appropriate matrix material, such as a paper, a fabric or a porous polymer. In some embodiments of the invention, this material is in fact the support upon which the electrochemical transistor device is arranged, so that the support forms an integral part of  
35 the operation of the device.

**Materials**

Preferably, the solidified electrolyte comprises a binder. It is preferred that this binder have gelling properties. The binder is preferably selected from the group consisting of gelatine, a gelatine derivative, 5 polyacrylic acid, polymethacrylic acid, poly(vinyl-pyrrolidone), polysaccharides, polyacrylamides, polyurethanes, polypropylene oxides, polyethylene oxides, poly(styrene sulphonic acid) and poly(vinyl alcohol) and 10 salts and copolymers thereof; and may optionally be cross-linked. The solidified electrolyte preferably further comprises an ionic salt, preferably magnesium sulphate if the binder employed is gelatine. The solidified electrolyte preferably further contains a 15 hygroscopic salt such as magnesium chloride to maintain the water content therein.

The organic material for use in the present invention preferably comprises a polymer which is electrically conducting in at least one oxidation state 20 and optionally further comprises a polyanion compound. Conductive polymers for use in the electrochemical transistor device of the invention are preferably selected from the group consisting of polythiophenes, polypyrroles, polyanilines, polyisothianaphthalenes, 25 polyphenylene vinylenes and copolymers thereof such as described by J C Gustafsson et al in Solid State Ionics, 69, 145-152 (1994); Handbook of Oligo- and Polythiophenes, Ch 10.8, Ed D Fichou, Wiley-VCH, Weinheim (1999); by P Schottland et al in Macromolecules, 33, 7051-7061 (2000); Technology Map Conductive Polymers, SRI Consulting (1999); by M Onoda in Journal of the 30 Electrochemical Society, 141, 338-341 (1994); by M Chandrasekar in Conducting Polymers, Fundamentals and Applications, a Practical Approach, Kluwer Academic Publishers, Boston (1999); and by A J Epstein et al in Macromol Chem, Macromol Symp, 51, 217-234 (1991). In an especially preferred embodiment, the organic material is

a polymer or copolymer of a 3,4-dialkoxythiophene, in which said two alkoxy groups may be the same or different or together represent an optionally substituted oxy-alkylene-oxy bridge. In the most preferred embodiment, the polymer is a polymer or copolymer of a 3,4-dialkoxythiophene selected from the group consisting of poly(3,4-methylenedioxythiophene), poly(3,4-methylenedioxythiophene) derivatives, poly(3,4-ethylenedioxythiophene), poly(3,4-ethylenedioxythiophene) derivatives, poly(3,4-propylenedioxythiophene), poly(3,4-propylenedioxythiophene) derivatives, poly(3,4-butylenedioxythiophene), poly(3,4-butylenedioxythiophene) derivatives, and copolymers therewith. The polyanion compound is then preferably poly(styrene sulphonate).

The support in some embodiments of the electrochemical transistor device of the present invention is preferably selected from the group consisting of polyethylene terephthalate; polyethylene naphthalene dicarboxylate; polyethylene; polypropylene; paper; coated paper, e.g. coated with resins, polyethylene, or polypropylene; paper laminates; paperboard; corrugated board; glass and polycarbonate.

The ion-selective layer in the first aspect of the invention may be formed of any ion-selective material. Preferred such ion-selective materials are ionophor-containing materials.

#### **Possible transistor architectures**

By patterning of the organic material of the electrochemically active element and of the contacts, electrode(s) and electrolyte in different ways, two main types of electrochemical transistor devices can be realised, upon which the electrochemical sensor devices of the present invention may be based. These main types, bi-stable and dynamic electrochemical transistor devices, will now be exemplified along with reference to figures thereof and an outline of their working principles.

Bi-stable transistor (type 1): Figures 1A and 1B schematically show one embodiment of a bi-stable transistor. The transistor comprises a source contact 1, a drain contact 2 and an electrochemically active element 3, which have all been formed from a continuous piece of organic material. Both the source and drain contacts are in electrical contact with an external power source, which allows the application of a voltage  $V_{ds}$  between them. The transistor further comprises a gate electrode 4, which can be formed from the same organic material as the source and drain contacts and the electrochemically active element. The gate electrode 4 is in electrical contact with an external power source, which allows applying a voltage  $V_g$  between the gate electrode and the electrochemically active element. This can be realised by applying  $V_g$  between the gate 4 and the source 1 or the drain 2, or directly between the gate 4 and the electrochemically active element 3. All of these organic material components have been deposited in one layer on a support 6. On top of this layer, covering part of the gate electrode 4 and the active element 3, is a layer of gel electrolyte 5. Furthermore, the gel electrolyte layer 5 is covered with an encapsulating layer 7 for prevention of solvent evaporation.

Working principle for the polarity of  $V_g$  shown in Figure 1, and in the case of an organic material which is conducting in its oxidised state and non-conducting when reduced to its neutral state: when a gate voltage  $V_g$  is applied between the gate electrode 4 and the electrochemically active element 3, the gate electrode is polarised positive (anode), and the electrochemically active element is polarised negative (cathode). This leads to onset of electrochemistry in the electrochemically active element and at the gate electrode; the organic material in the transistor channel is reduced at the same time as an oxidation reaction takes place at the gate electrode. The reduced material

in the transistor channel displays a drastically diminished electrical conductivity, which results in the closure of the transistor channel and an effective reduction of the current between source and drain for a given source-drain voltage  $V_{ds}$ , i.e. the transistor is in an "off" mode. When the external circuit supplying voltage to the gate electrode and the electrochemically active element is broken, the oxidation state of the transistor channel is maintained. No reversal of the electrochemical reactions is possible because of the interruption by electrolyte 5 of electron flow between gate electrode 4 and electrochemically active element 3.

Thus, the bi-stable transistor has a memory-function: It is possible to switch on or off the transistor channel with short pulses of gate voltage,  $V_g$ , applied to the gate. The respective conductivity states remain when gate voltage is removed (a zero-power device). Further adjustments of conduction characteristics in the electrochemically active element, or resetting thereof to the initial, high conductivity mode, can be performed by applying different voltages to the gate electrode.

Dynamic transistor: Figures 2A and 2B schematically show a dynamic transistor. The transistor comprises a source contact 1, a drain contact 2 and an electrochemically active element 3, which have all been formed from a continuous piece of organic material. The electrochemically active element 3 comprises a transistor channel 3a and a redox sink volume 3b. Both the source and drain contacts are in electrical contact with an external power source, which allows the application of a voltage  $V_{ds}$  between them. The transistor further comprises two gate electrodes 4a and 4b arranged on either side of the electrochemically active element 3. The gate electrodes can be formed from the same organic material as the source and drain contacts and the electrochemically active element. The gate electrodes are

in electrical contact with an external power source, which allows application of a voltage  $V_g$  between them. All of these organic material components have been deposited in one layer on a support 6. On top of this layer, covering parts of the gate electrodes 4a and 4b and the active element 3, is a layer of gel electrolyte 5. Furthermore, the gel electrolyte layer 5 is covered with an encapsulating layer 7 for prevention of solvent evaporation.

Working principle for the polarity of  $V_g$  shown in Figure 2, and in the case of an organic material which is conducting in its oxidised state and non-conducting when reduced to its neutral state: when a gate voltage  $V_g$  is applied between the gate electrodes 4a and 4b, gate electrode 4a is polarised positive (anode), and gate electrode 4b is polarised negative (cathode). This leads to onset of electrochemistry in the electrochemically active element; the organic material in the transistor channel 3a (adjacent to gate electrode 4a) is reduced, while the organic material in the redox sink volume 3b (adjacent to gate electrode 4b) is oxidised. These electrochemical reactions require an internal transfer of electrons within the electrochemically active element. Electrons that are released in the oxidation reaction in the redox sink volume migrate to the transistor channel, where they replenish the electrons consumed in the reduction of organic material occurring in this segment of the electrochemically active element. The reduced volume in the transistor channel displays a drastically diminished electrical conductivity, which results in the closure of the transistor channel and an effective reduction of the source-drain current for a given source drain voltage  $V_{ds}$ , i.e. the transistor is "off". When the external circuit applying voltage to the gate electrodes 4a and 4b is broken, a spontaneous discharge occurs, in that electrons flow from the reduced material in the transistor channel to the oxidised material in the redox



sink volume, until the original redox state is re-established within the electrochemically active element. For maintenance of overall charge neutrality, this flow of electrons within the electrochemically active element  
5 is accompanied by an ion flow within the solidified electrolyte.

Bi-stable transistor (type 2): Figures 3A and 3B schematically show another embodiment of a bi-stable transistor, the architecture of which is based on the  
10 dynamic transistor architecture described immediately above. With reference to Figures 3A and 3B, this embodiment of a bi-stable transistor has the same components as said dynamic transistor, the difference being that the layer of solidified electrolyte 5 is  
15 patterned, forming two separate segments of electrolyte 5a and 5b. This patterning has the effect of interrupting ion flow within the electrolyte, which interruption in turn means that no spontaneous reversal of electrochemical reactions can occur between transistor  
20 channel 3a and redox sink volume 3b. In similarity to the case of the first bi-stable transistor device described above, the oxidation state of the transistor channel is maintained when the external circuit, here supplying voltage to the gate electrodes, is broken.

25 The sensor devices of the present invention may utilise any of the basic transistor architectures outlined above, and may also utilise diode architectures whose construction will be readily conceivable for the skilled man in light of the description of transistors  
30 herein and Example 2 below. An exemplary figure of a sensor device according to the first aspect of the invention is given as Figure 6. The basic transistor architecture is as explained above in relation to Figure 1, corresponding reference numerals referring to  
35 corresponding components. In addition to what is shown in Figure 1, the sensor device comprises an ion-selective

layer 8, through which may pass only ionic species the detection of which is desired.

The invention will be further illustrated by the following non-limiting description of examples. Example 1 describes experiments conducted on two different transistors upon which a sensor device according to the invention may be based. Example 2 is a description of experiments conducted on a humidity sensor according to the invention. In Example 2, two different sensor architectures have been realised. One of these is based on a transistor device, while the other is based on a diode device.

#### Example 1 - Electrochemical transistors

##### Experiments

Bi-stable (type 1) and dynamic transistors were realised by patterning films of partially oxidised poly(3,4-ethylenedioxythiophene) with poly(styrene sulphonate) as counterions (frequently referred to as PEDOT:PSS in the present text) into a T-shaped structure. The design followed the schematic drawings of the bi-stable and dynamic transistors presented in Figures 1 and 2, respectively. In its pristine, partially oxidised state, PEDOT:PSS films are conductive, providing the opportunity of modulating the current in the transistor channel by reduction of the PEDOT:PSS electrochemically. All processing and material handling was done in ambient atmosphere.

Patterning through screen-printing: PEDOT:PSS was applied as a thin film on a polyester carrier, Orgacon<sup>TM</sup> EL - 300Ω/square, as provided by AGFA. Conducting patterns were generated using a screen-printed deactivation paste: Orgacon-Strupas gel, as provided by AGFA, was mixed with an aqueous sodium hypochlorite solution, resulting in a concentration of the active

degradation agent of approximately 1.2%. Printing was performed using a manual screen printing board (Movivis, purchased from Schneider) using a screen with 77 lines/cm mesh. After 1 minute, the deactivation agent was removed from the PEDOT:PSS film by washing thoroughly with copious amounts of water.

Deposition of source and drain contacts and gate electrode(s): After patterning of the PEDOT:PSS film, silver-paste (DU PONT 5000 Conductor) was printed on top of the PEDOT:PSS areas that form the drain and source contacts and gate electrode(s). Alternatively, the transistors can be entirely made of organic materials by locally increasing the layer thickness of the PEDOT:PSS in the gate, source and drain areas by drying-in of a PEDOT-PSS solution (Baytron P™ from Bayer) onto these areas. Such all-organic transistors were successfully realised on polyester foils.

Deposition of gelled electrolyte: Calcium chloride (2%), iso-propanol (35%), and gelatine (10%) (Extraco gelatine powder 719-30) were dissolved in de-ionised water at approximately 50°C (weight percentages of the resulting gel in parenthesis). Structures of gelled electrolyte on patterned PEDOT:PSS film were formed by printing the gel on top of the PEDOT:PSS film. The thickness of the gelled electrolyte ranged from 20 to 100 µm. Gelled electrolyte structures were realised at line widths down to 300 µm. Screen-printing of gelled electrolyte was performed using a 32 mesh screen. The distance between the drain and source contacts was typically 1 to 2 mm.

Encapsulation: The gelled electrolyte was coated with a waterproof coating, such as plastic paint or foils, encapsulating the device. Shelf lifetimes of several months were achieved.

Electrical characterisation: All testing was performed in ambient atmosphere at room temperature. Current-voltage (I-V) transistor curves were measured

with a HP Parameter Analyzer 4155 B, in combination with an external HP E3631A power supply.

### Results

5        Bi-stable transistor: A bi-stable transistor such as that shown schematically in Figures 1A and 1B was realised. The bi-stable transistor had a transistor channel width of 600  $\mu\text{m}$  and a gel width of 800  $\mu\text{m}$ , with a transistor channel of 0.48  $\text{cm}^2$ . However, smaller  
10 dimensions were also successfully tested using photolithographic photoresist patterning in combination with reactive ion plasma etching. These devices exhibited channel widths ranging from 5 to 20  $\mu\text{m}$  and a gel width of 20  $\mu\text{m}$ .

15        Typically, the gate voltages  $V_g$  applied to the gate electrode were in the interval between 0 V and 0.7 V. Drain-source characteristics were determined by sweeping the source-drain voltage from 0 V to 2 V. The resulting I-V curves are displayed in Figure 4.

20        Characteristic switching times for the conductivity modulation were determined by applying a square shaped modulation voltage (alternating between 0 V and 1 V) and measuring the resulting current changes. Typical rise and decline times (defined as the time required for a 90%  
25 increase respectively decrease of the current level) were determined as 0.1 s and 0.2 s, respectively.

On/Off ratios (defined as the current ratio  $I_{ds,max}/I_{ds,min}$  at a source-drain voltage  $V_{ds}$  of 2 V for  $V_g = 0$  V(on) and  $V_g = 0.7$  V(off)) reached 15000. Figure 4  
30 displays the output characteristics of the bi-stable transistor,  $I_{ds}$  vs  $V_{ds}$  for different gate voltages.

The inset in Figure 4 shows the source-drain current  $I_{ds}$  as a function of the gate voltage  $V_g$  for a constant source-drain voltage  $V_{ds}$  ( $V_{ds} = 2$  V). From these curves,  
35 an important parameter, the trans-conductance  $g_m$ , can be evaluated.  $g_m$  is defined as:

27

$$g_m = \frac{\delta I_{ds}}{\delta V_g} (V_{ds} = \text{constant})$$

The value of the trans-conductance of the bi-stable transistor device was found to be -1.2 mA/V.

Dynamic transistor: A dynamic transistor such as  
 5 that shown schematically in Figures 2A and 2B was realised. The dynamic transistor had a channel width of 250  $\mu\text{m}$  and a gel width of 900  $\mu\text{m}$ , with a transistor channel of 0.23  $\text{cm}^2$ . However, smaller dimensions of PEDOT and gel patterns down to 4  $\mu\text{m}$  were successfully reached  
 10 using photolithographic patterning. These devices exhibited channel widths ranging from 4 to 20  $\mu\text{m}$  and a gel width of 20  $\mu\text{m}$ .

Typically, the gate voltages  $V_g$  applied to the gate electrodes spanned an interval of 0 V to 3 V. On/Off  
 15 ratios (defined as the current ratio  $I_{ds, \text{max}}/I_{ds, \text{min}}$  at a source-drain voltage  $V_{ds}$  of 2 V for  $V_g = 0$  V (on) and  $V_g = 3$  V (off)) reached 1000. Figure 5 displays the output characteristics of the dynamic transistor,  $I_{ds}$  vs  $V_{ds}$  for different gate voltages.

20 The inset in Figure 5 shows the source-drain current  $I_{ds}$  as a function of the gate voltage  $V_g$  for a constant source-drain voltage  $V_{ds}$  ( $V_{ds} = 2$  V). From these curves, the value of the trans-conductance of the dynamic transistor device was found to be -0.10 mA/V.

25

## **Example 2 - Humidity sensors**

### **Experiments**

30 The electrolyte used in these experiments was NAFION. NAFION is a material that changes its ion-conductivity with the humidity. At low humidity, NAFION has almost no ionic conductivity, but at greater humidity the ion conduction increases around 10 orders of  
 35 magnitude. The mobility of cations in NAFION increases with increasing humidity.

Processing:

Manufacturing of the device can either be done by regular photolithography in combination with dry etching  
5 or by cutting the structure with a plotter. The structures were based on Orgacon™ EL, 300  $\Omega$ /square.

Structures were manufactured by photolithography and dry etching as described in Example 1. For definition of the area for the proton conductor or electrolyte, the  
10 following steps were followed:

- On top of the remaining structures of PEDOT:PSS a UV-sensitive layer of SU-8 was spin-coated.
- The SU-8 layer was pre-baked in oven for 15  
15 minutes.
- The SU-8 layer was exposed through a mask defining the pattern.
- The SU-8 layer was post-baked in oven for 5 minutes.
- The SU-8 layer was developed with regular  
20 developer for SU-8.

This gave rise to an opening through the layer of SU-8 defining the area for the proton conductor. The  
25 proton conductor was then drop-casted in the opening defined by SU-8. The proton conductor was baked in oven at 80°C for 10 minutes. Silver paint was printed onto the source, drain and gate contacts to achieve better contacts.

30 Alternatively, a plotter can be used with a sharp knife to define the device structure of PEDOT:PSS. The knife is cutting through the PEDOT:PSS layer but not through the underlying plastic foil in the Orgacon™ foil. The result is areas that have no direct connection to  
35 each other.

- The area for the proton conductor is defined by cutting an opening in a plastic foil with glue on one side.
- The foil is glued onto the patterned structure of PEDOT:PSS.
- The device is run through a laminator to achieve better adhesion between the plastic foil and the PEDOT:PSS layer.
- The proton conductor is drop-casted in the opening defined by plastic foil.
- The proton conductor is baked in oven at 80°C for 10 minutes.
- Silver paint is printed onto the anode and cathode contacts to achieve better contacts.

#### Measurement results

##### Transistor structure:

Modulation of the current for the transistor structure is done as described in Example 1 above. In the present humidity-sensing device, the proton conductor works as electrolyte. The change in ion conduction within the proton conductor gives rise to change of modulation of the current between source and drain at a certain applied gate voltage.

##### Diode structure:

When the humidity is changed, ion conduction is changed within the NAFION material, which gives rise to a change of de-doping of the channel in the diode at the applied gate voltage. The cathode has a lower potential than the anode, which results in a de-doping of the channel. This occurs since the area of the channel which is close to the cathode and in contact with the proton conductor has a lower potential than the area which is close to the anode and in contact with the proton conductor.

The measurements were done with a HP Parameter-analyser, and the humidity was changed using a climate chamber. The diagrams shown in Figure 8 are based on  
5 static measurements of the current through the transistor and the diode. For the transistor, this was done by application of a constant gate voltage and measurement of the variation in current between source and drain, at constant voltage, with the humidity. For the diode, this  
10 was done by application of a constant voltage between anode and cathode and measurement of how the current varies with the humidity. The cathode had a lower potential than the anode. The potential applied to the diode was 2 V and the potentials applied to the  
15 transistor were  $V_{ds} = -1$  V and  $V_g = 0.5$  V. The relative humidity was increased and decreased in increments of 5%. The temperature in the chamber was held constant (25°C) during the measurements.



## CLAIMS

1. A supported or self-supporting electrochemical sensor device comprising:

- 5       - a source contact,
- a drain contact,
- at least one gate electrode,
- an electrochemically active element arranged between, and in direct electrical contact with,  
10       the source and drain contacts, which electrochemically active element comprises a transistor channel and is of a material comprising an organic material having the ability of electrochemically altering its conductivity  
15       through change of redox state thereof,
- an ion-selective layer comprising a material which is selective for at least one ionic species, which layer is in direct electrical contact with the electrochemically active element, and  
20       - a solidified electrolyte in direct electrical contact with the ion-selective layer and said at least one gate electrode and interposed between them in such a way that electron flow between the electrochemically active element and said gate  
25       electrode(s) is prevented,

whereby flow of electrons between source contact and drain contact is controllable by means of a voltage applied to said gate electrode(s), and controllable by means of a change in concentration of said ionic species  
30   in the solidified electrolyte.

2. An electrochemical sensor device according to claim 1, in which said source and drain contacts, gate electrode(s) and electrochemically active element are  
35   arranged in one common plane.

3. An electrochemical sensor device according to claim 2, in which the source contact, the drain contact and the gate electrode(s) form a T-shaped configuration.

5        4. An electrochemical sensor device according to any one of the preceding claims, in which a continuous or interrupted layer of said solidified electrolyte covers the ion-selective layer and covers at least partially said gate electrode(s).

10

5. An electrochemical sensor device according to any one of the preceding claims, in which the sensor device is arranged as a diode device.

15        6. An electrochemical sensor device according to any one of the preceding claims, in which at least one of said source and drain contacts and gate electrode(s) is formed from the same material as the electrochemically active element.

20

7. An electrochemical sensor device according to claim 6, in which all of said source and drain contacts and gate electrode(s) are formed from the same material as the electrochemically active element.

25

8. An electrochemical sensor device according to any one of claims 6-7, in which the source and drain contacts and the electrochemically active element are formed from a continuous piece of said material comprising an organic material.

30

9. An electrochemical sensor device according to any one of the preceding claims, in which said transistor channel retains its redox state upon removal of the gate voltage.

35

10. An electrochemical sensor device according to any one of claims 1-8, in which said transistor channel spontaneously returns to its initial redox state upon removal of the gate voltage.

5

11. An electrochemical sensor device according to claim 10, in which the electrochemically active element further comprises a redox sink volume adjacent to the transistor channel, the device comprising at least two  
10 gate electrodes arranged on opposite sides of the electrochemically active element so that one gate electrode is closer to the transistor channel and one gate electrode is closer to the redox sink volume.

12. An electrochemical sensor device according to any one of the preceding claims, in which said organic material is a polymer.

13. An electrochemical sensor device according to  
20 claim 12, in which said polymer material is selected from the group consisting of polythiophenes, polypyrroles, polyanilines, polyisothianaphtalenes, polyphenylene vinylenes and copolymers thereof.

14. An electrochemical sensor device according to  
25 claim 13, in which said polymer material is a polymer or copolymer of a 3,4-dialkoxythiophene, in which said two alkoxy groups may be the same or different or together represent an optionally substituted oxy-alkylene-oxy  
30 bridge.

15. An electrochemical sensor device according to claim 14, in which said polymer or copolymer of a 3,4-dialkoxythiophene is selected from the group consisting of  
35 poly(3,4-methylenedioxythiophene), poly(3,4-methylenedioxythiophene) derivatives, poly(3,4-ethylenedioxythiophene), poly(3,4-ethylenedioxythiophene) derivatives,

poly(3,4-propylenedioxythiophene), poly(3,4-propylenedioxythiophene) derivatives, poly(3,4-butylenedioxythiophene), poly(3,4-butylenedioxythiophene) derivatives, and copolymers therewith.

5

16. An electrochemical sensor device according to any one of the preceding claims, in which said organic material further comprises a polyanion compound.

10

17. An electrochemical sensor device according to claim 16, in which said polyanion compound is poly(styrene sulphonic acid) or a salt thereof.

15

18. An electrochemical sensor device according to any one of the preceding claims, in which said solidified electrolyte comprises a binder.

20

19. An electrochemical sensor device according to claim 18, in which said binder is a gelling agent selected from the group consisting of gelatine, a gelatine derivative, polyacrylic acid, polymethacrylic acid, poly(vinylpyrrolidone), polysaccharides, polyacrylamides, polyurethanes, polypropylene oxides, polyethylene oxides, poly(styrene sulphonic acid) and poly(vinyl alcohol), and salts and copolymers thereof.

25

20. An electrochemical sensor device according to any one of the preceding claims, in which said solidified electrolyte comprises an ionic salt.

30

21. An electrochemical sensor device according to any one of the preceding claims, which is self-supporting.

35

22. An electrochemical sensor device according to any one of claims 1-20, which is arranged on a support.

23. An electrochemical sensor device according to claim 22, in which said support is selected from the group consisting of polyethylene terephthalate, polyethylene naphthalene dicarboxylate, polyethylene, 5 polypropylene, polycarbonate, paper, coated paper, resin-coated paper, paper laminates, paperboard, corrugated board and glass.

24. A process for the production of a supported 10 electrochemical sensor device comprising:

- a source contact,
- a drain contact,
- at least one gate electrode,
- an electrochemically active element arranged 15 between, and in direct electrical contact with, the source and drain contacts, which electrochemically active element comprises a transistor channel and is of a material comprising an organic material having the ability of 20 electrochemically altering its conductivity through change of redox state thereof,
- an ion-selective layer comprising a material which is selective for at least one ionic species, which layer is in direct electrical contact with the 25 electrochemically active element, and
- a solidified electrolyte in direct electrical contact with the ion-selective layer and said at least one gate electrode and interposed between them in such a way that electron flow between the 30 electrochemically active element and said gate electrode(s) is prevented,

which process comprises deposition of said contacts, electrode(s), electrochemically active element, ion-selective layer and electrolyte onto a support.

35

25. A process according to claim 24, wherein said contacts, electrode(s), electrochemically active element,

ion-selective layer and/or electrolyte are deposited by means of printing techniques.

26. A process according to claim 24, wherein said  
5 contacts, electrode(s), electrochemically active element, ion-selective layer and electrolyte are deposited by means of coating techniques.

27. A process according to any one of claims 24-26,  
10 in which device said organic material comprises a polymer, which process comprises deposition of said polymer on a support through *in situ* polymerisation.

28. A process according to any one of claims 24-27  
15 comprising patterning of any one of said contacts, electrode(s) and electrochemically active element using a subtractive method.

29. A process according to claim 28, in which said  
20 patterning is performed through chemical etching.

30. A process according to claim 28, in which said patterning is performed through gas etching.

25 31. A process according to claim 28, in which said patterning is performed by mechanical means, comprising scratching, scoring, scraping and milling.

32. A process according to any one of claims 24-31,  
30 in which said supported electrochemical sensor device is as defined in any one of claims 2-20 and 22-23.

33. A supported or self-supporting electrochemical sensor device comprising:

- 35
- a source contact,
  - a drain contact,
  - at least one gate electrode,

- an electrochemically active element arranged between, and in direct electrical contact with, the source and drain contacts, which electrochemically active element comprises a transistor channel and is of a material comprising an organic material having the ability of electrochemically altering its conductivity through change of redox state thereof,
  - a solidified electrolyte in direct electrical contact with the electrochemically active element and said at least one gate electrode and interposed between them in such a way that electron flow between the electrochemically active element and said gate electrode(s) is prevented, which solidified electrolyte comprises a material whose ion transport behaviour is responsive to a change in an environmental parameter,
- whereby flow of electrons between source contact and drain contact is controllable by means of a voltage applied to said gate electrode(s), and controllable by means of a change in said environmental parameter.

34. An electrochemical sensor device according to claim 33, said solidified electrolyte comprising a material whose ion transport behavior is responsive to a change in one or more environmental parameters chosen from a group comprising humidity, temperature, light, pressure, air concentration of a gaseous contaminant, and ion concentration.

30

35. An electrochemical sensor device according to any one of claims 33 and 34, further comprising an ion-selective layer comprising a material which is selective for at least one ionic species, which layer is in direct electrical contact with the solidified electrolyte, and which layer is operative to interact with the solidified

electrolyte to enable response to said environmental parameter.

36. An electrochemical sensor device according to  
5 claim 35, in which the ion-selective layer is in direct electrical contact with the electrochemically active element and is interposed between the solidified electrolyte and the electrochemically active element.

10 37. An electrochemical sensor device according to claim 35, in which the ion-selective layer serves as an interface between the solidified electrolyte and an environment surrounding the sensor device.

15 38. An electrochemical sensor device according to any one of claims 33-36, in which said source and drain contacts, gate electrode(s) and electrochemically active element are arranged in one common plane.

20 39. An electrochemical sensor device according to any one of claims 33-38, in which the source contact, the drain contact and the electrode(s) form a T-shaped configuration.

25 40. An electrochemical sensor device according to any one of claims 33-39, in which a continuous or interrupted layer of said solidified electrolyte covers the ion-selective layer and covers at least partially said gate electrode(s).

30 41. An electrochemical sensor device according to any one of claims 33-40, in which the sensor device is arranged as a diode device.

35 42. An electrochemical sensor device according to any one of claims 33-41, in which at least one of said source and drain contacts and gate electrode(s) is formed



from the same material as the electrochemically active element.

43. An electrochemical sensor device according to  
5 any one of claims 33-42, in which all of said source and drain contacts and gate electrode(s) are formed from the same material as the electrochemically active element.

44. An electrochemical sensor device according to  
10 any one of claims 42-43, in which the source and drain contacts and the electrochemically active element are formed from a continuous piece of said material comprising an organic material.

15 45. An electrochemical sensor device according to any one of claims 33-44, in which said transistor channel retains its redox state upon removal of the gate voltage.

46. An electrochemical sensor device according to  
20 any one of claims 33-44, in which said transistor channel spontaneously returns to its initial redox state upon removal of the gate voltage.

47. An electrochemical sensor device according to  
25 claim 46, in which the electrochemically active element further comprises a redox sink volume adjacent to the transistor channel, the device comprising at least two gate electrodes arranged on opposite sides of the electrochemically active element so that one gate  
30 electrode is closer to the transistor channel and one gate electrode is closer to the redox sink volume.

48. An electrochemical sensor device according to  
any one of claims 33-47, in which said organic material  
35 is a polymer.

49. An electrochemical sensor device according to claim 48, in which said polymer material is selected from the group consisting of polythiophenes, polypyrroles, polyanilines, polyisothianaphtalenes, polyphenylene  
5 vinylenes and copolymers thereof.

50. An electrochemical sensor device according to claim 49, in which said polymer material is a polymer or copolymer of a 3,4-dialkoxythiophene, in which said two  
10 alkoxy groups may be the same or different or together represent an optionally substituted oxy-alkylene-oxy bridge.

51. An electrochemical sensor device according to claim 50, in which said polymer or copolymer of a 3,4-di-  
15 alkoxythiophene is selected from the group consisting of poly(3,4-methylenedioxythiophene), poly(3,4-methylenedioxythiophene) derivatives, poly(3,4-ethylenedioxythiophene), poly(3,4-ethylenedioxythiophene) derivatives,  
20 poly(3,4-propylenedioxythiophene), poly(3,4-propylenedioxythiophene) derivatives, poly(3,4-butylenedioxythiophene), poly(3,4-butylenedioxythiophene) derivatives, and copolymers therewith.

25 52. An electrochemical sensor device according to any one of claims 33-51, in which said organic material further comprises a polyanion compound.

53. An electrochemical sensor device according to claim 52, in which said polyanion compound is  
30 poly(styrene sulphonic acid) or a salt thereof.

54. An electrochemical sensor device according to any one of claims 33-53, in which said solidified  
35 electrolyte comprises a binder.

55. An electrochemical sensor device according to claim 54, in which said binder is a gelling agent selected from the group consisting of gelatine, a gelatine derivative, polyacrylic acid, polymethacrylic acid, poly(vinylpyrrolidone), polysaccharides, polyacrylamides, polyurethanes, polypropylene oxides, polyethylene oxides, poly(styrene sulphonic acid) and poly(vinyl alcohol), and salts and copolymers thereof.

56. An electrochemical sensor device according to any one of claims 33-55, in which said solidified electrolyte comprises an ionic salt.

57. An electrochemical sensor device according to any one of claims 33-56, which is self-supporting.

58. An electrochemical sensor device according to any one of claims 33-56, which is arranged on a support.

59. An electrochemical sensor device according to claim 58, in which said support is selected from the group consisting of polyethylene terephthalate, polyethylene naphthalene dicarboxylate, polyethylene, polypropylene, polycarbonate, paper, coated paper, resin-coated paper, paper laminates, paperboard, corrugated board and glass.

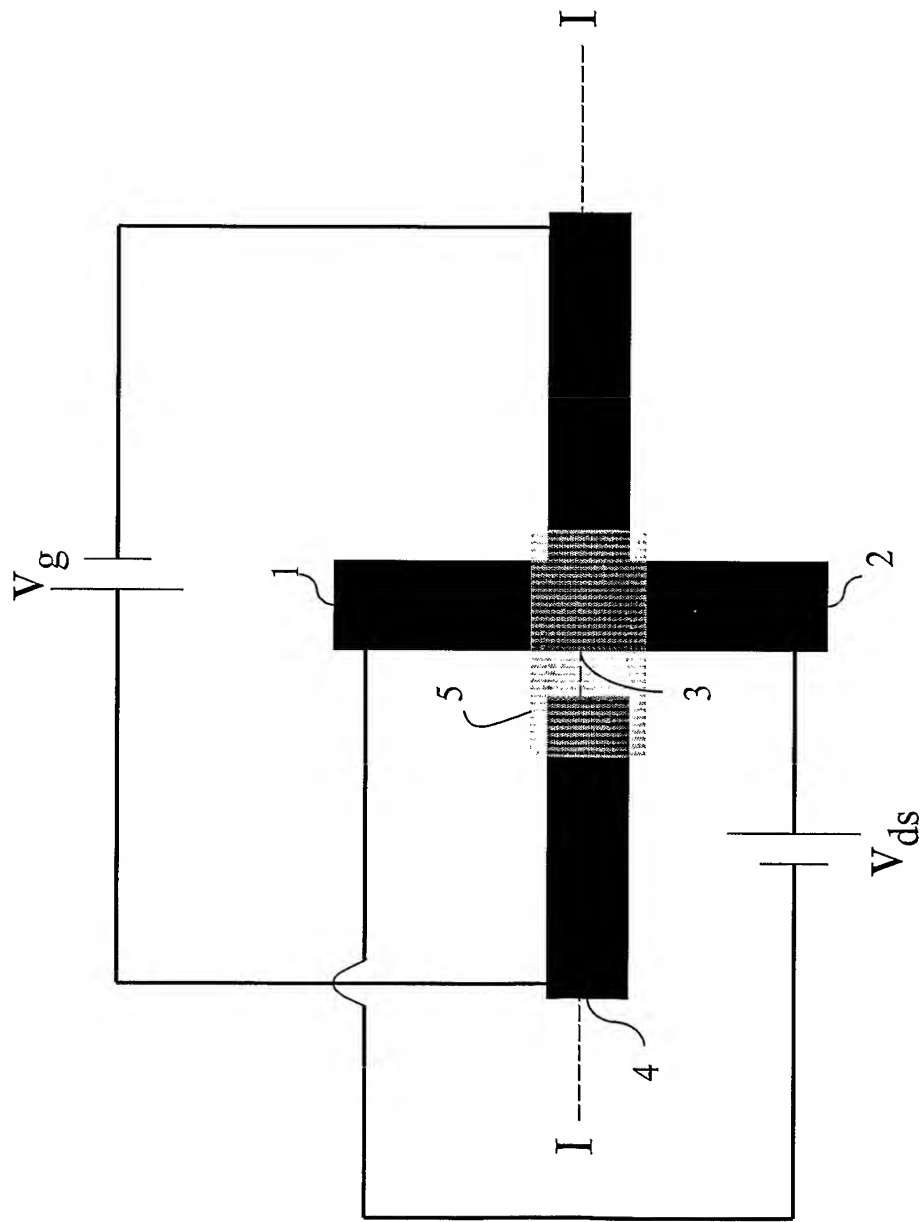


FIGURE 1A

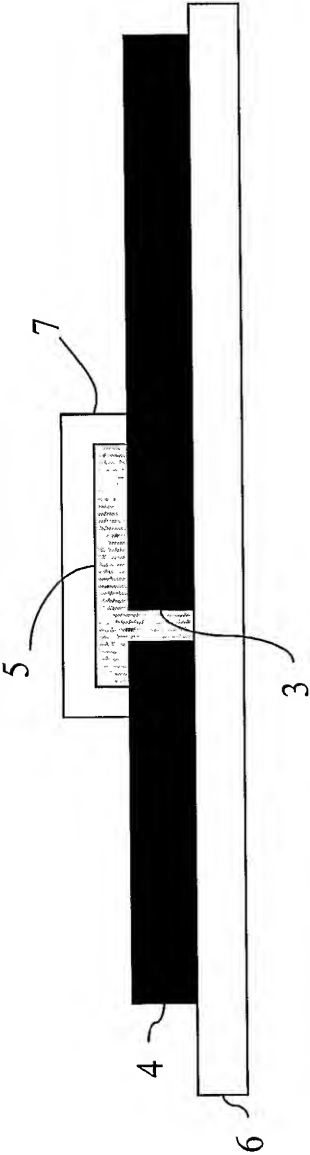


FIGURE 1B

3/13

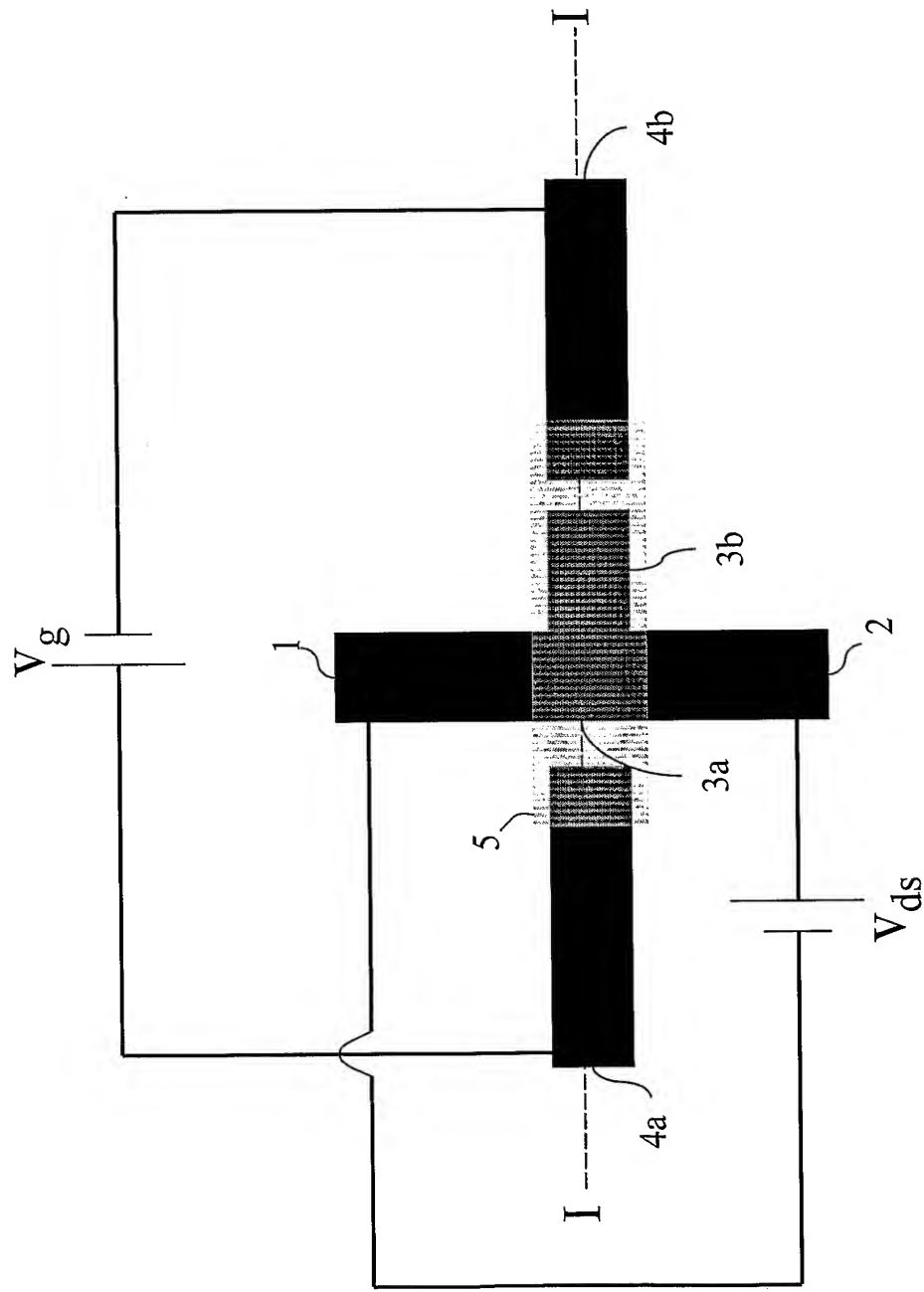


FIGURE 2A

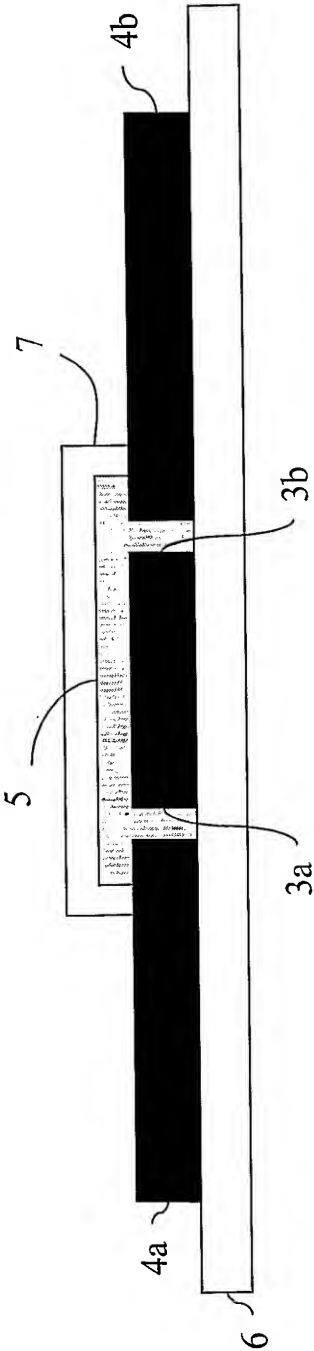


FIGURE 2B

5/13

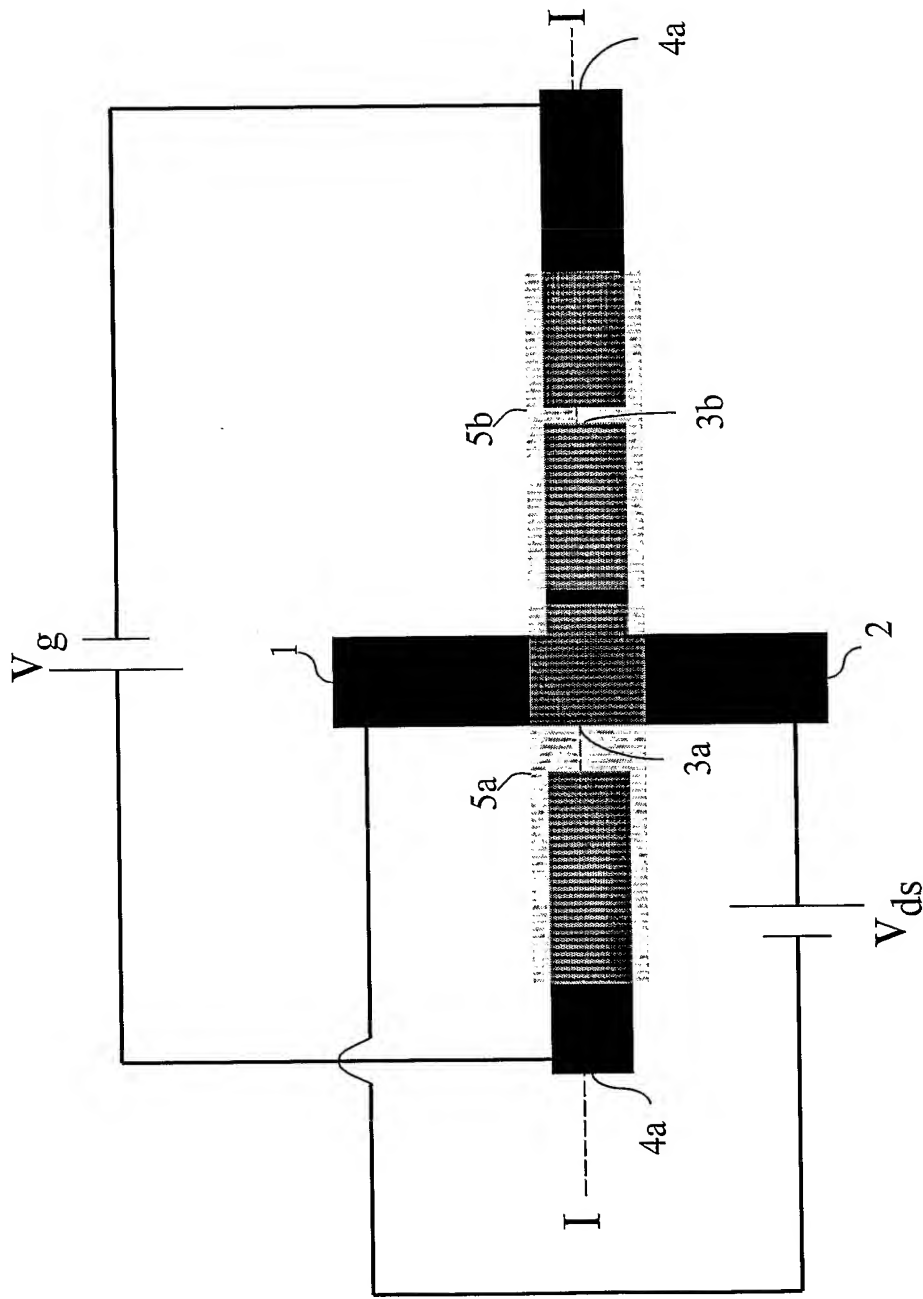


FIGURE 3A



6/13

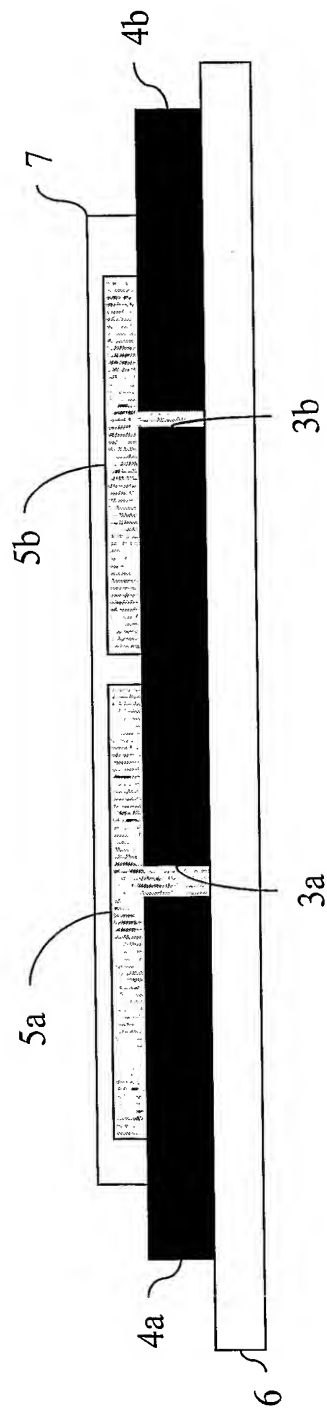


FIGURE 3B

7/13

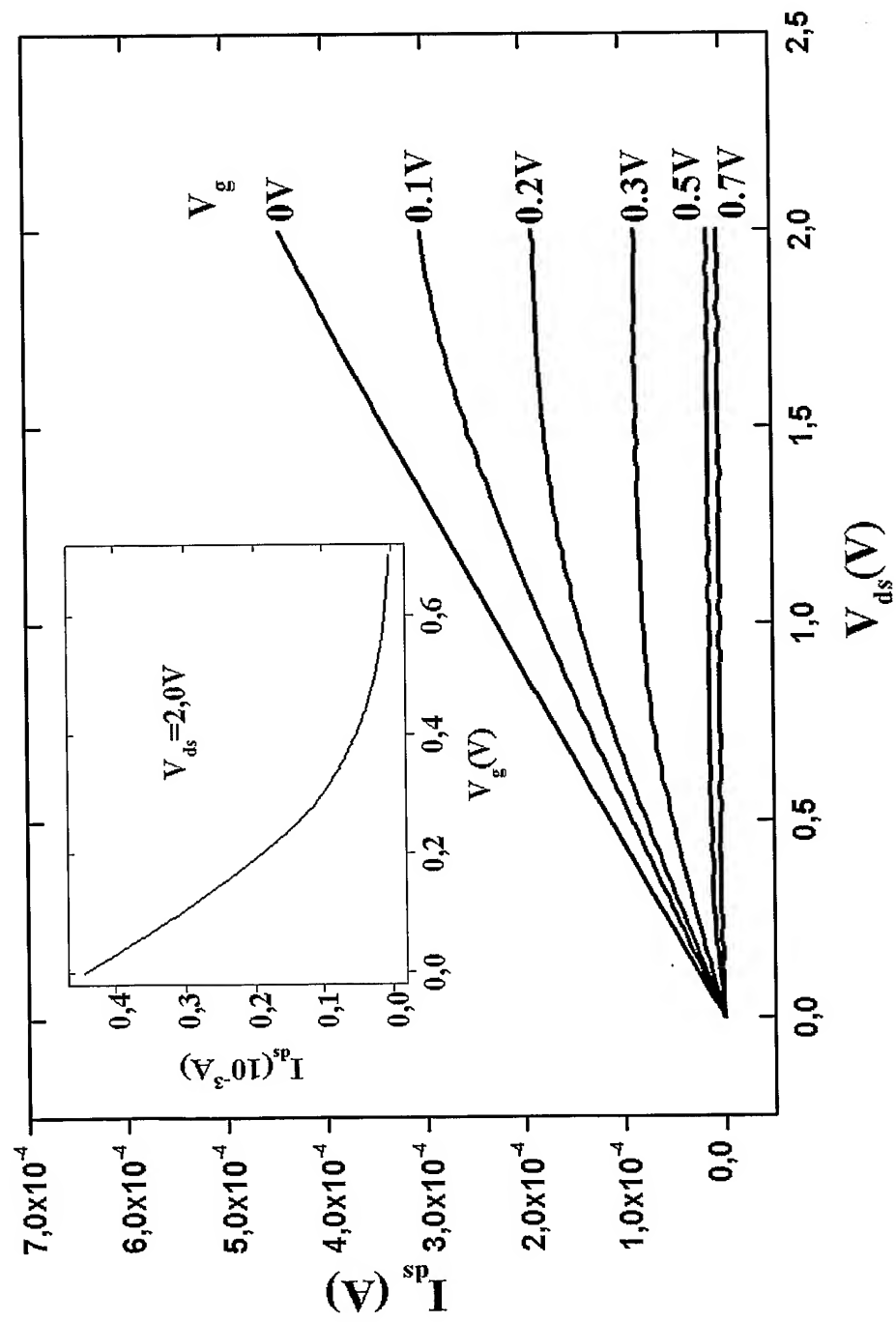


FIGURE 4

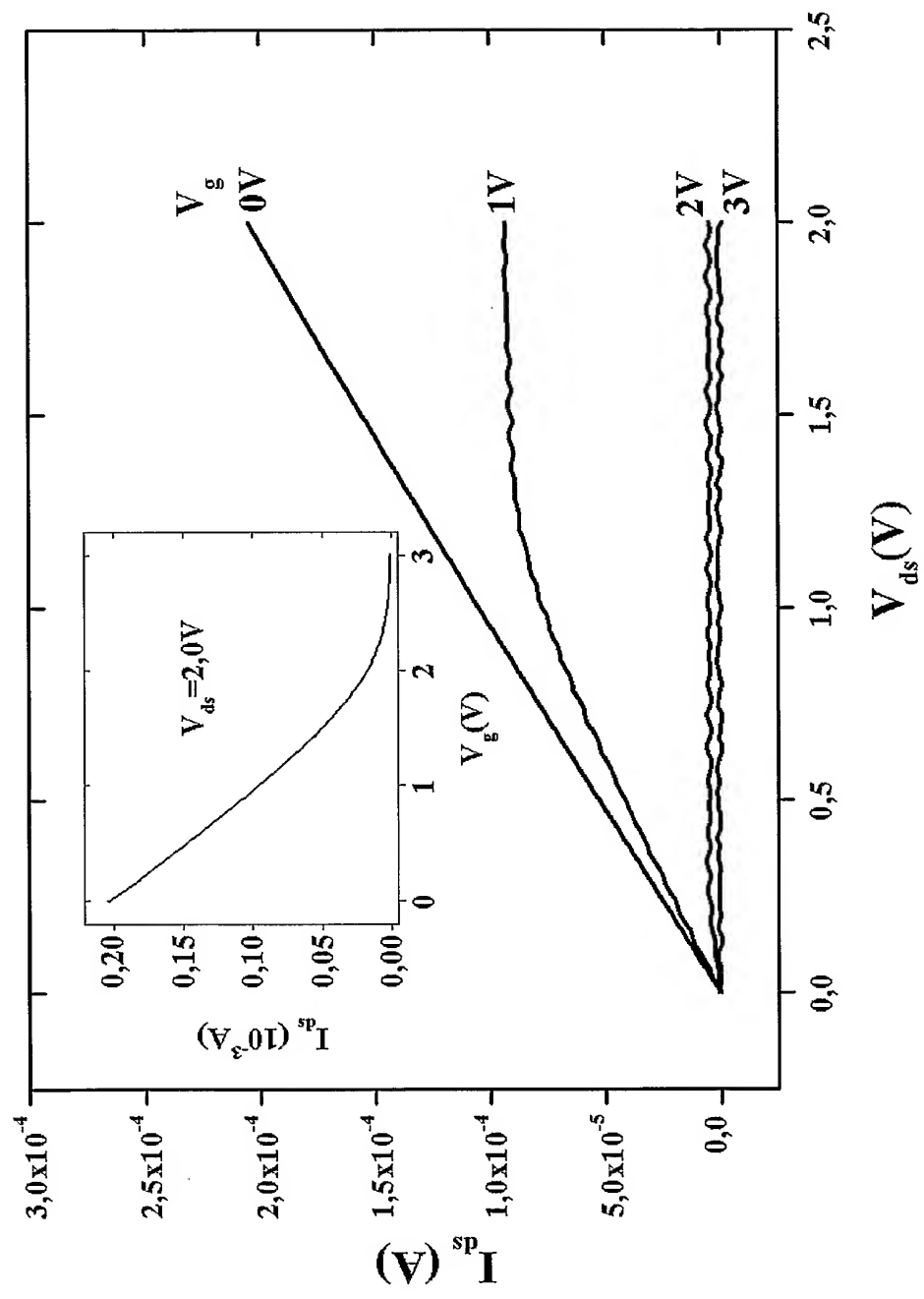


FIGURE 5

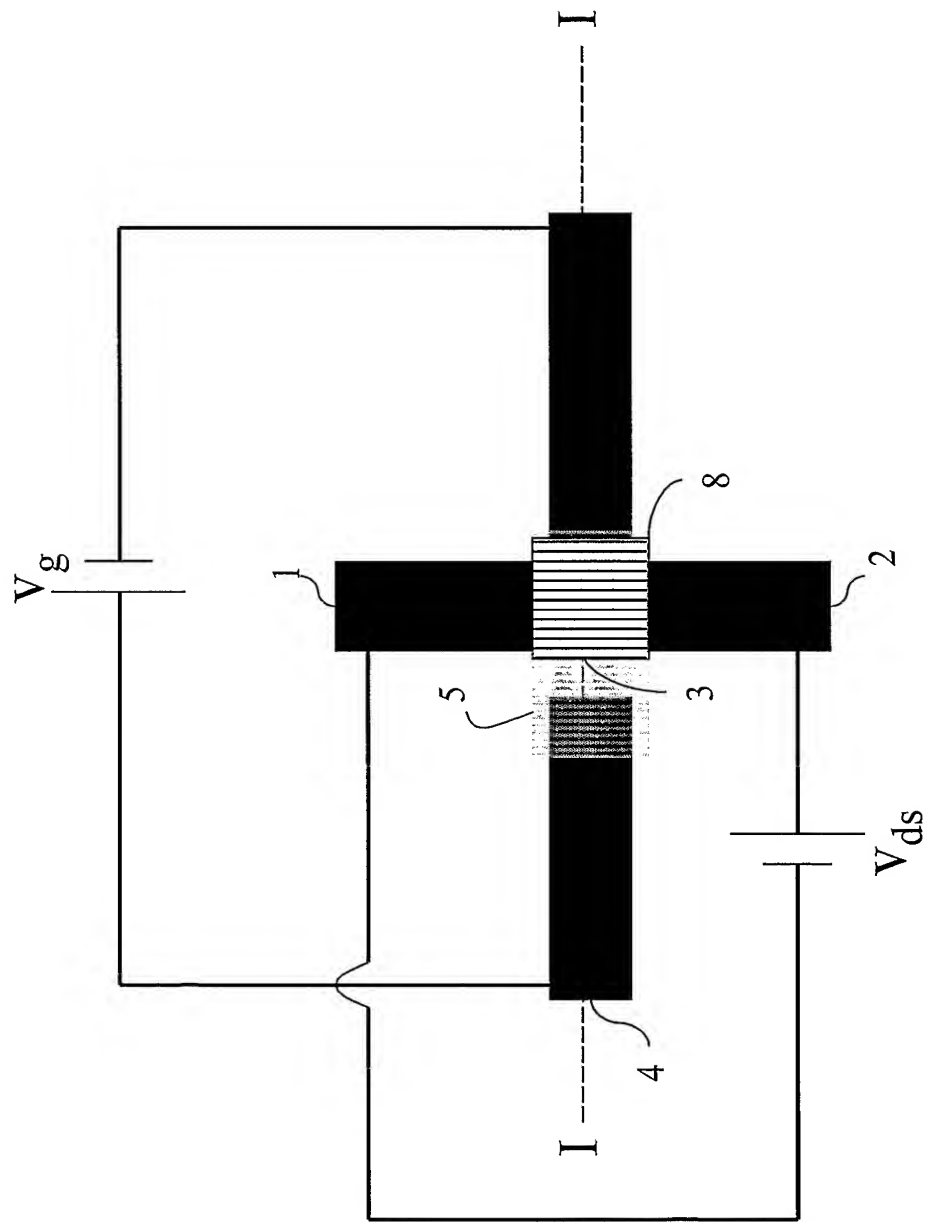


FIGURE 6A

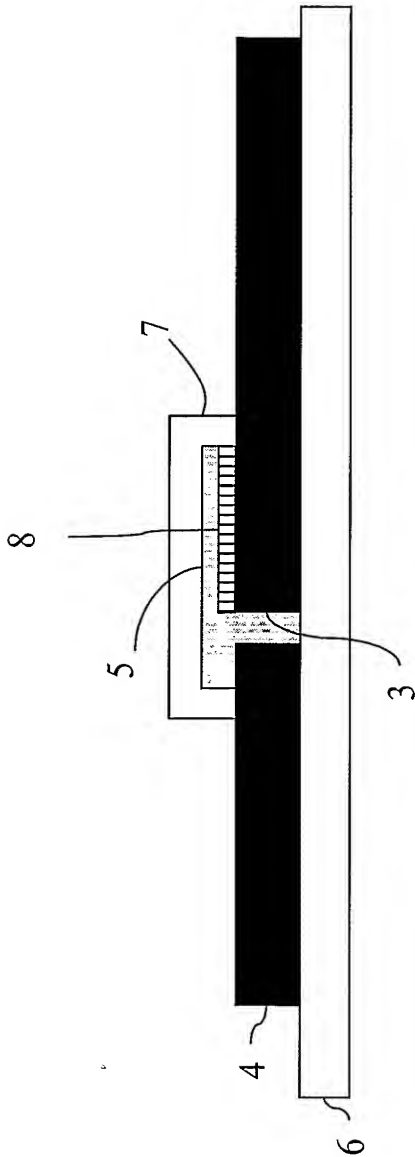


FIGURE 6B

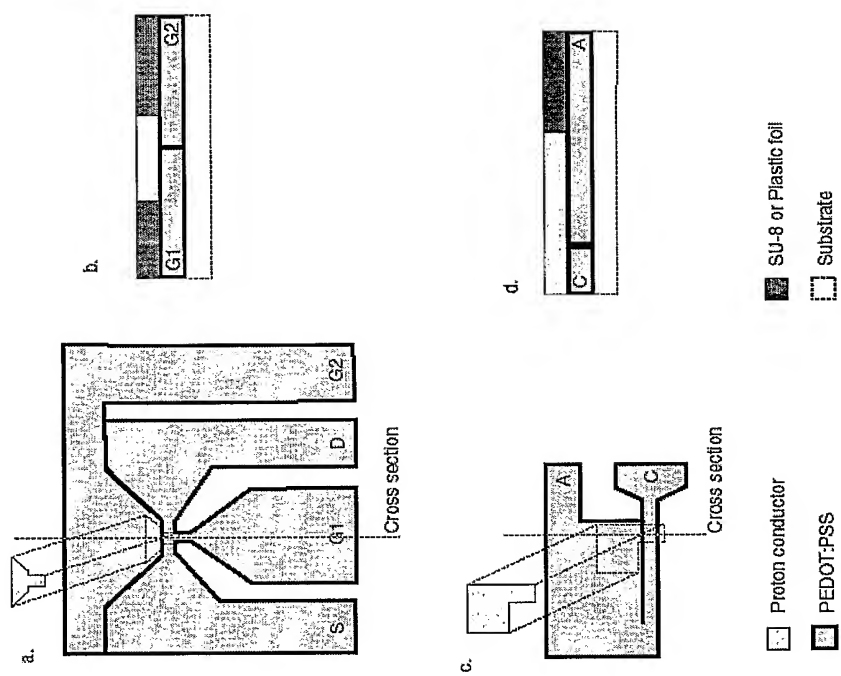


FIGURE 7

12/13

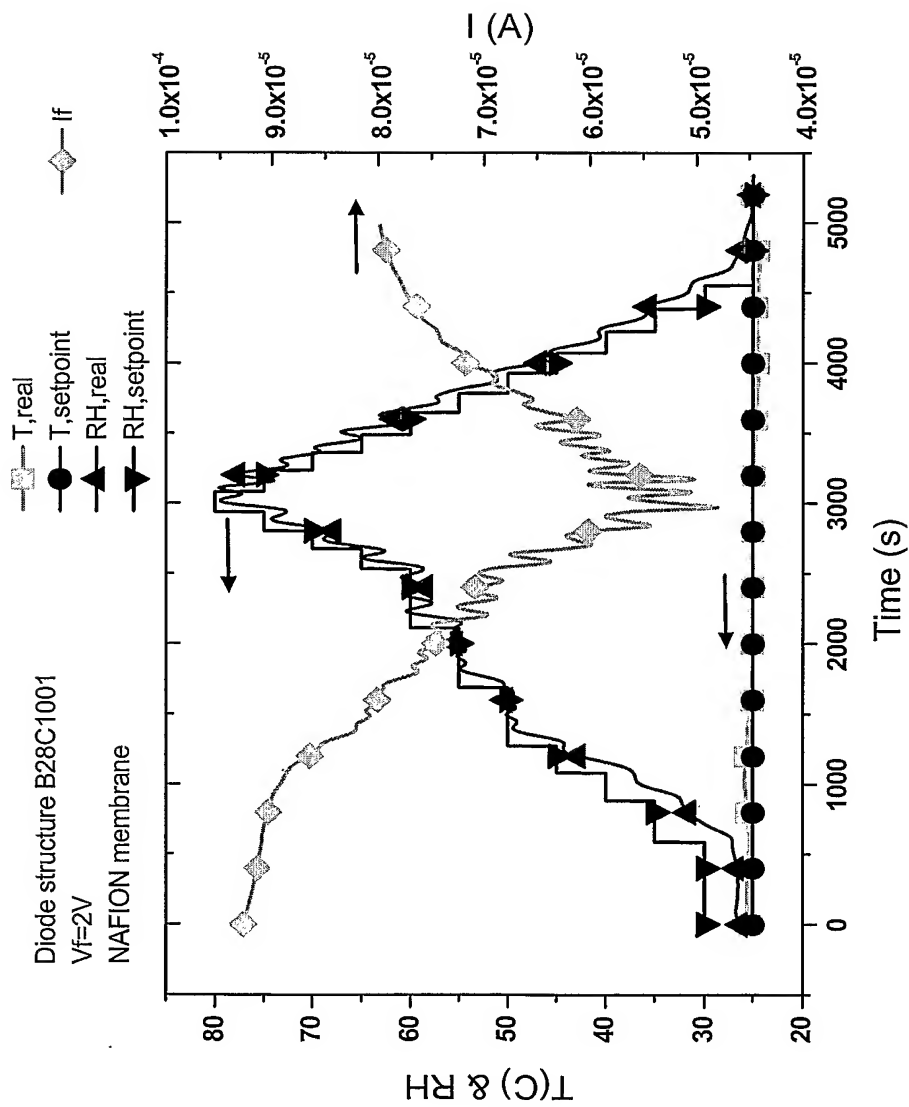


FIGURE 8A

13/13

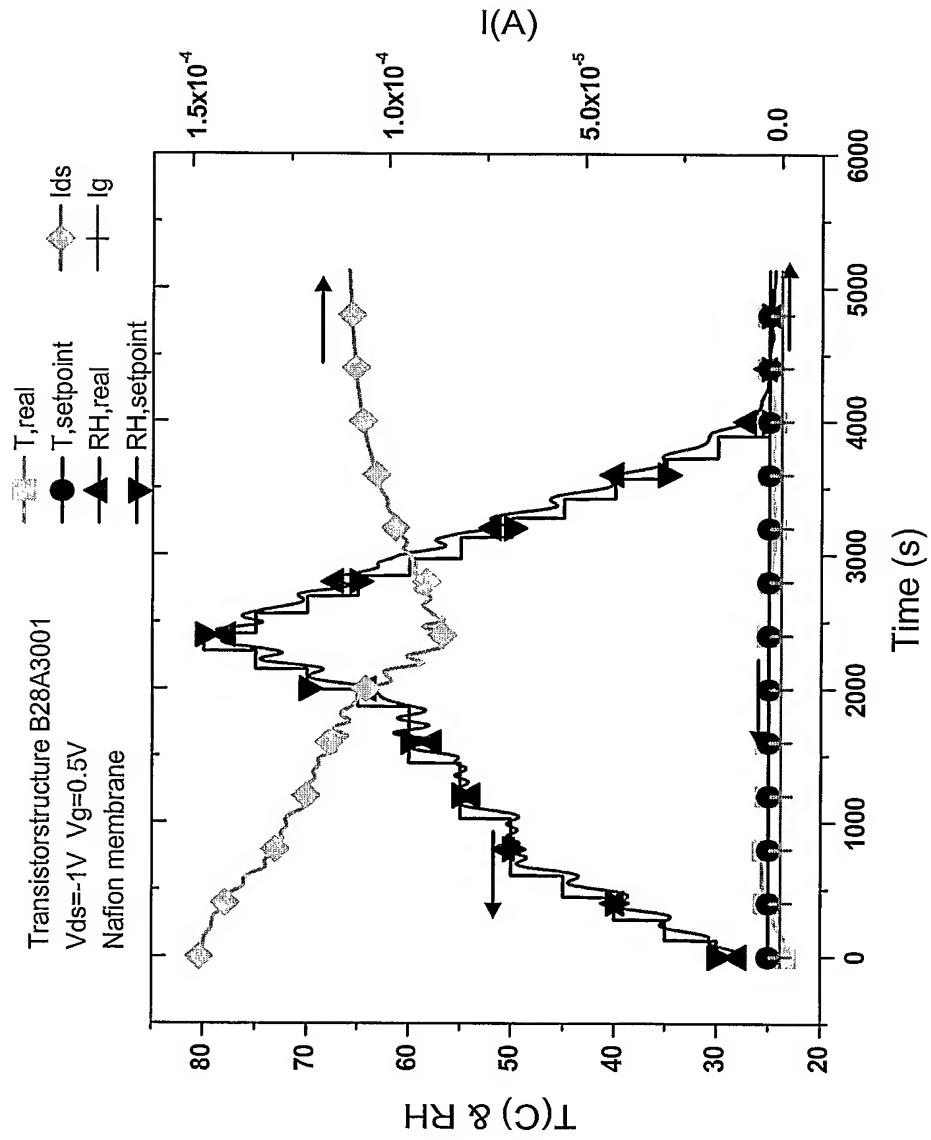


FIGURE 8B



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 02/02210

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: G01N 27/414, H01L 51/20, H01L 51/40

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: G01N, H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0478380 A1 (KABUSHIKI KAISHA TOSHIBA), 1 April 1992 (01.04.92), page 2, line 1 - page 3, line 15; page 17, line 40 - page 18, line 30  --	1-59
A	WO 9841853 A1 (AROMASCAN PLC), 24 Sept 1998 (24.09.98), page 2, line 1 - page 5, line 10  -- -----	1-59

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

29 November 2002

Date of mailing of the international search report

12 -02- 2003

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 02/02210

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				JP	4137666 A	12/05/92
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				GB	9705278 D	00/00/00
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